Effective thermal-oxidative reclamation of waste tire rubbers for producing high-performance rubber composites

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ABSTRACT: The disposal and accumulation of waste tire rubbers have caused significantly negative impact on the circular economy and sustainable environment. To reuse and recycle the ground tire rubber (GTR), we developed a thermal-oxidative reclamation process using a newly designed dynamic reclamation reactor. In the absence of any chemical agent, a high scission efficiency was achieved at a sol fraction of 66.53 wt% at 200 °C after 20 min from the thermal oxidation of GTR. The physical and chemical structural evolution of GTR during the thermo-oxidation process were systemically investigated by monitoring the Mooney viscosity, sol-gel ratio, molecular weight and chemical structure changes. The reclaimed ground tire rubber (RGTR) containing ultrafine fillers and soluble elastomer can be easily dispersed into a natural rubber (NR) matrix. The mechanical properties and aging resistance of the modified NR were enhanced

with the RGTR addition up to 40 wt%. This work demonstrates a green and up-scalable approach for reclamation and reuse of waste tire rubbers for sustainable rubber industry.

KEYWORDS: Ground tire rubber, Thermal-oxidative reclamation, High scission, Natural rubber, Mechanical properties

INTRODUCTION

The rubber industry makes a significant contribution to the world economy, but the abundant and indiscriminate disposal of industrial rubber products, such as waste tires, has raised significant environmental and economic challenges globally. There are around 1 billion end-of-life tires are generated annually and is expected to reach 1.2 billion by 2030.[1, 2] More than 50% of the waste tires are disposed into landfill and incineration, which has caused serious environmental pollution and hazards to eco-systems, therefore, landfilling has been prohibited by the European Commission and many other countries since 1999.[3] There still lack effective strategies in dealing with the waste tire rubbers due to their chemically stable and robust covalent crosslinking polymer networks, it is of great importance to explore more effective and environmentally-friendly technologies to reclaim and reuse these solid waste rubbers.

Reclamation of ground tire rubber (GTR) can partially break the polymer network and derive useful materials out of the waste rubbers, such as drainage materials in road construction, bitumen modifiers for road-asphalt mixtures and rubber processing additives.[4-7] However, the current reclamation processes generally produce up to 20 wt% of soluble rubber at high energy cost, and leave the majority to be tightly bounded with carbon black (CB) in clusters. This prevents the dispersion of the reclaimed ground tire rubber (RGTR) in rubber processing, and results in poor mechanical reinforcement effect.[8, 9] High scission of crosslinked rubbers with a high scission efficiency (>50 wt% soluble rubber) is highly desirable in order to facilitate the dispersion of RGTR and the associated CB in rubber matrices for high performance rubber products.[10, 11]

Traditional reclamation of GTR include mechanical,[12-14] mechano-chemical,[15-17] thermo-mechanical and thermo-chemical,[18, 19] or other physical and chemical methods.[20-23] To further improve the reclamation degree with a high content of soluble rubber for ultrafine dispersion, Tripathy *et al*. reclaimed vulcanized natural rubber (NR) by a "high-pressure high-temperature sintering (HPHTS)" method and obtained a viscous reclaimed rubber at high temperature (310 °C) for 1 h under nitrogen, but this process involved high energy consumption and operational hazards.[24] Shi *et al*. reclaimed GTR by a co-rotating twin-screw extruder at 300 °C, using pine tar as the chemical agent, the liquid reclaimed rubber produced by this process were used as reactive polymeric plasticizer in NR to replace conventional aromatic oil.[25] Disulfide oil,[26] dipropyl disulfide and bis (3-triethoxysilyl propyl) tetrasulfide[27] were also applied to facilitate the degradation of GTR during mechanochemical processes. These additional chemicals effectively improved the degree of reclamation and decreased the crosslink density of GTR. However, the applications of these odorous chemicals, as desulfurization agents or softeners under high temperatures, have caused further environmental pollution. To achieve high reclamation efficiency and low emissions in the rubber-reclaiming industry, eco-friendly and feasible processes are urgently needed.

Thermal-oxidation aging has the potential to be applied to the reclamation of rubber vulcanizates. It has been recognized that a rapid combination with oxygen is a characteristic reaction of the unsaturated double bonds of main chains at high temperatures, which can cause a high degree of chain scission.[28] Moreover, in chemically crosslinked diene rubbers, the chemical bonding energy of sulfur-sulfur bonds (S-S, 270 kJ/mol) is much weaker than that of carbon-sulfur bonds (C-S, 310 kJ/mol), or carbon-carbon bonds (C-C, 370 kJ/mol). Hence, the sulfide linkages in vulcanized rubber are susceptible to thermal-oxidative treatment.[29] Modrow *et al*.[30] identified the rupture of sulfur crosslinks during thermal-oxidation aging and provided a qualitative description of the reaction channels involved. Compared with the reclamation methods mentioned above, the thermal-oxidation could be a simple process with high capacity and relatively low cost. Furthermore, the thermal-oxidative process is environmentally friendly, without involving harmful chemicals.

In this study, a facile and environmentally-friendly dynamic thermal-oxidative approach was employed to reclaim GTR under an air atmosphere. The reclamation degree was evaluated using a custom-designed dynamic thermal-oxidative reactor at 200 °C as a function of stirring time. The structural evolution and morphology of the reclaimed rubber with different reclamation degrees were investigated using gel fraction analysis, Fourier transform infrared (FTIR) analysis, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The reclaimed materials were applied as processing modifiers for NR and the mechanical properties and aging resistance of the modified NR were investigated.

EXPERIMENTAL SECTION

Materials. GTR powder with an average particle size of 40 meshes was generated from truck tires, kindly supplied by Jiangsu Zhonghong Environment Technology Co, Ltd. (China). The composition of the heavy truck tire is 33% of CB, 40% of NR, 13% of synthetic rubber, such as butadiene rubber (BR) and styrene-butadiene rubber (SBR). Rubber ingredients, including stearic acid, zinc oxide, accelerator CZ (N-cyclohexyl benzothiazole-2-sulphenamide) and sulfur were commercial grades.

Dynamic Thermal-oxidative Reclamation of GTR. Reclamation was carried out in a self-designed tank reactor with adjustable pulse air input at 200 °C for four different oxidative time periods, 5 min (RGTR-1), 10 min (RGTR-2), 15 min (RGTR-3), and 20 min (RGTR-4), which resulted in RGTRs with four reclamation degrees. The output gas was collected and incinerated. The details of the equipment and operation procedures are shown in Figure 1.

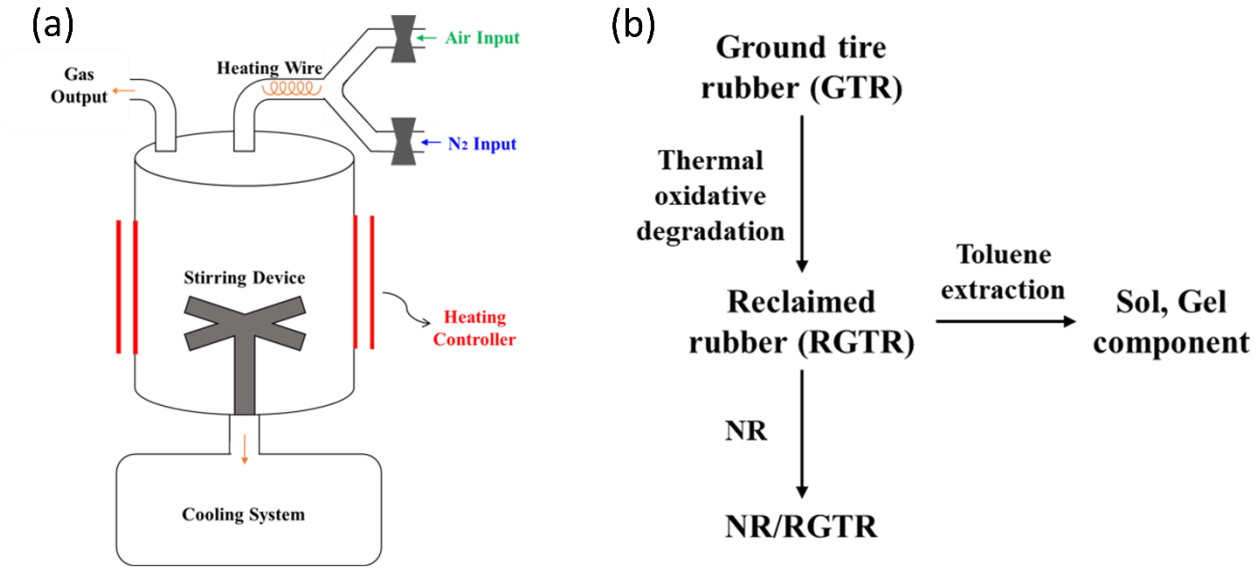

Figure 1. (a) Schematic diagram of the experimental apparatus for thermal-oxidative reclamation, (b) experimental flowchart.

Characterization of RGTRs. The sol fractions of RGTRs were measured with a Soxhlet extraction method using toluene as the solvent. The samples were refluxed in toluene for 72 h and then dried at 60 °C in vacuum to constant weight after 4 h. The weights of the samples before and after the treatment were recorded. The sol fraction (S_f) was calculated according to $S_f = \frac{m_0-(m_1+m_s)}{m_0\times\omega} \times 100\%$, where m_0 is the mass of samples before extraction, m_1 is the mass of the dried samples after extraction, and m_s is the mass of the soluble materials in the GTR, the ω is the rubber content.

The molecular weight and distribution of the sol of both GTR and RGTR were characterized with a HLC-8320 Gel Permeation Chromatography Instrument, using tetrahydrofuran (THF) as the solvent at room temperature. The calibration was done against polystyrene standards.

The crosslink density was determined by immersing small pieces of the samples in toluene for 72 h at room temperature to allow equilibrium swelling. The samples were then taken out, removing the solvent from the surface, and weighed immediately. The crosslink density was calculated using

the Flory-Rehner equation.[31] Due to the presence of filler, a modified Kraus correction factor C (C=1.11 for CB) was used.[32]

Mooney viscosity of the RGTR was measured according to standard ASTM D1646-2017 by a Mooney viscometer (MZ-4016B, Jiangsu Mingzhu Testing Machinery Co., Ltd., China).

RGTRs with different reclamation degrees were analysed with FTIR (Spectrum 100) in the absorbance range 4000-400 cm^{-1} in a reflection mode.

The composition of the gel component was determined using a Thermal Gravimetric Analyzer (Discovery TGA550). The measurement was conducted in a temperature range of 50-900 °C (50-550 °C under a nitrogen atmosphere and 550-900 °C under air) at a heating rate of 20 °C /min.

Preparation of NR/RGTR composites. NR and RGTR were composited in different formulations according to Table 1 and 2 using a two-roll mill at room temperature. RGTR was first masticated with NR for 2 min, followed by mixing with the activating agents (stearic acid and zinc oxide) for 1 min, accelerator CZ was then added to form a masterbatch, sulfur was added finally. The concentrations of the additives were based on 100 parts by weight of rubber. After storing at ambient temperature for 24 h, the samples were vulcanized at 140 °C. The experimental process is shown in Figure 1b.

Table 1. Formulation of NR/RGTRs composites (Values in wt%)

Samples	NR/GTR	NR/RGTR-1	NR/RGTR-2	NR/RGTR-3	NR/RGTR-4	NR
RGTR	40	40	40	40	40	-
NR	60	60	60	60	60	100
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2
CBS	0.8	0.8	0.8	0.8	0.8	0.8
Stearic acid	0.34	0.34	0.34	0.34	0.34	0.34
Zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5

Table 2 Formulation of NR/RGTR-3 composites (Values in wt%)

Samples	NR	NR/10R GTR	NR/20R GTR	NR/30R GTR	NR/40R GTR	NR/50R GTR	NR/60R GTR	NR/70R GTR
NR	100	90	80	70	60	50	40	30
RGTR30	0	10	20	30	40	50	60	70
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
CBS	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Stearic acid	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Characterization of NR/RGTRs. The mechanical properties of the samples were tested with an Instron 4465 Universal Testing Machine at a speed of 500 mm/min, the specimen dimensions are 25 × 4 × 2.0 mm^3. The tensile strength, elongation-at-break, modulus at 100, 200 and 300% elongation were determined.

The fractured surfaces of the NR/RGTRs were vacuum-plated with a thin layer of gold for electrical conduction and then were observed with a Phenom Pro scanning electron microscopy at 10 kV.

The accelerated thermal aging resistance was determined by heating the samples at 100 °C for 48 h, with forced air circulation. A laminar air flow was maintained through the heating chamber. The dumbbell-shaped specimens were placed with the smallest surface, facing towards the air flow in order to avoid the disturbance from the air flow. The tensile strength, stress (fracture strength) at elongation-at-break, modulus at 100, 200 and 300% elongation were determined for the vulcanized rubber after aging.

RESULTS AND DISCUSSION

Characterization of RGTRs. The effectiveness of the thermal-oxidative reclamation process was evaluated by measuring the sol fraction of the RGTRs via a Soxhlet extraction method. As shown in Figure 2a, the sol fraction of RGTRs increases significantly with the stirring time and reached 66.5% after 20 min (RGTR-4). These results indicate that the crosslinked rubber network of GTR can be effectively destructed by the dynamic thermal-oxidative reclamation process in the presence of air at 200 °C.

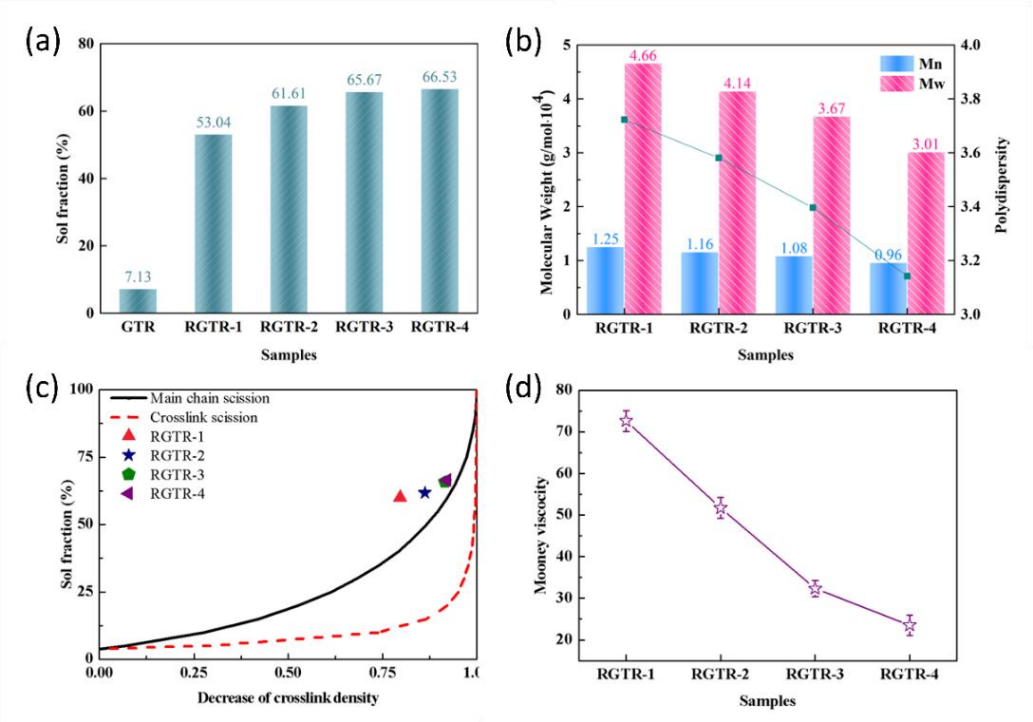

Figure 2. (a) The sol fraction of different RGTRs as a function of stirring time, (b) Molecular weight and polydispersity of different RGTRs, (c) Horikx's curves: the sol fraction as a function of crosslink density, (d) Mooney viscosity of different RGTRs.

As shown in Figure 2b, the M_n of sol in RGTR is of the order of 10^4 or lower, and decreases slightly with the increase of stirring time, while the M_w decreases significantly. However, the virgin NR in the GTR has an initial molecular weight (M_n) in the range of 1.0×10^5 to 2.5×10^6 g/mol. The crosslinked structure in GTR was destroyed to an extent related to the reclamation degree. Increasing stirring time led to a lower molecular weight of the rubber, *i.e.*, the polymer chains became shorter.

To differentiate the nature of the reclamation, *i.e.*, either crosslink network scission or main chain scission, we further applied Horikx's theory[33] to investigate the reclamation reactions. Theoretical Horikx's curves along with the experimental data points are presented in Figure 2c. The analysis considered that the experimental points located near the lower curve (dash line) correspond to a more selective crosslink scission, while those located near the upper curve (solid line) correspond to main chain scission. The points between the two curves undergo reclaiming, a combination between crosslink scission and main chain scission. As shown in Figure 2c, the experimental points are all positioned above the main chain scission curve, meaning that the reclamation is dominated by main chain scission under high temperatures. In addition, extending stirring time moved the points up to the right, indicating more efficient reclamation at longer stirring time. In the thermal-oxidative reclamation process, the presence of oxygen at 200 °C helped generate a high sol fraction in RGTR and led to scission of the main chain predominantly.

Mooney viscosity of the elastomeric composites is a measure of the processability, which is determined by the structure and composition of the reclaimed rubber. Figure 2d shows that the Mooney viscosity decreases with the devulcanization extent, which is desired for these materials to be used as additives for rubber processing.

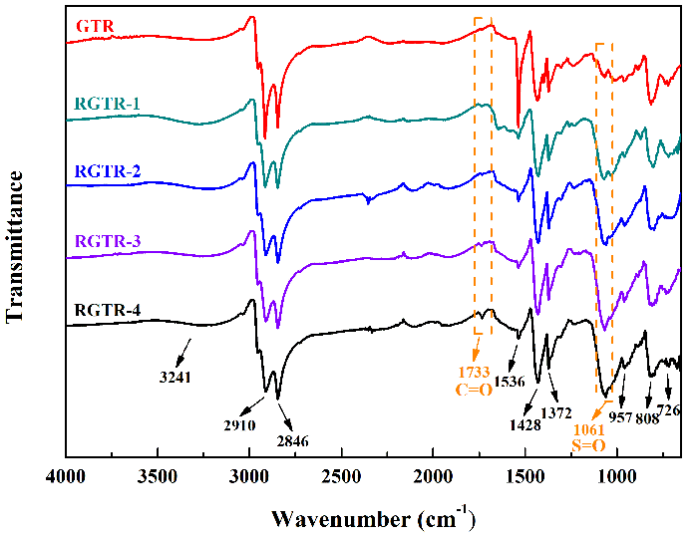

Figure 3. FTIR spectra of GTR and RGTRs.

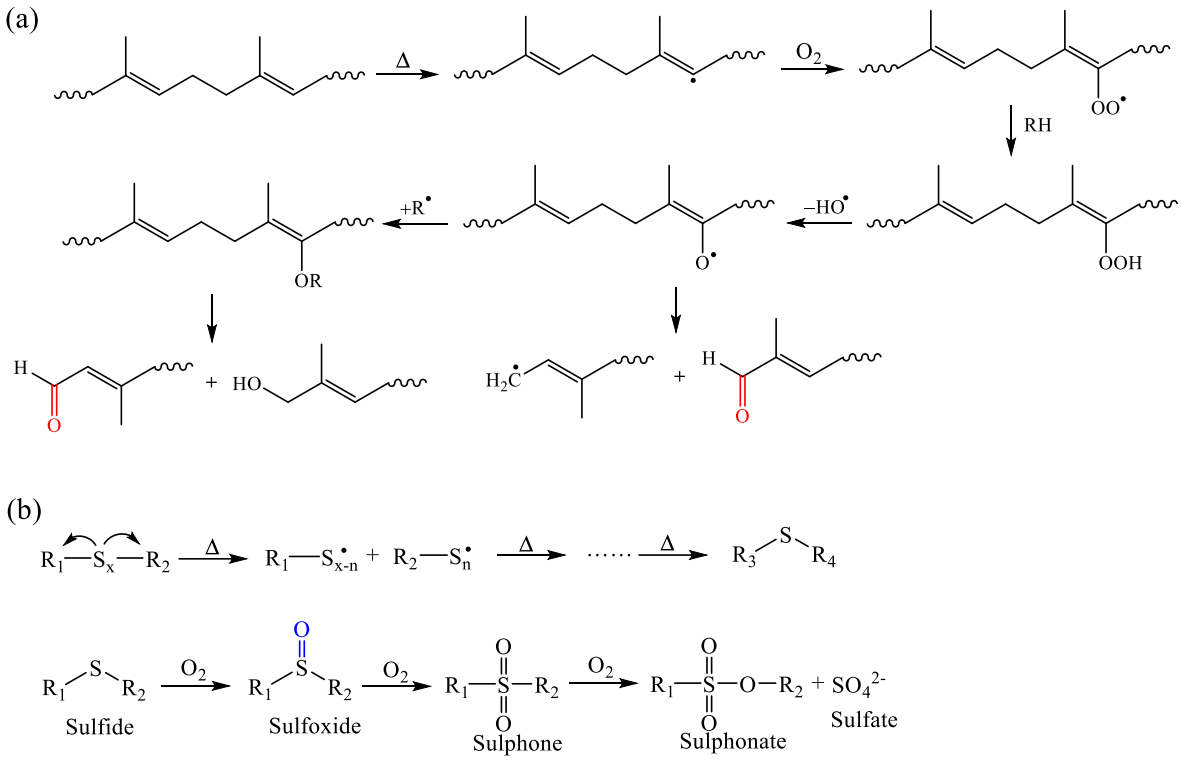

Figure 4. Oxidative reclamation reaction, (a) on the main chains and (b) on the crosslinks.

The macromolecular structure of the GTR during the thermal-oxidative reclamation was investigated using FTIR spectroscopy, the results are given in Figure 3. During the thermal-oxidative process at 200 °C, new absorbances in the region of 1733 cm^{-1} and 1060 cm^{-1} are observed in RGTRs as compared to GTR. The new peak at 1060 cm^{-1} is assigned as the sulfoxide (-S=O), which confirms that partial sulfur-containing crosslink bonds are cleaved during thermal-oxidative reclamation and sulfur-containing groups are formed as a result of the complex reactions with oxygen in the presence of air. The intensity of the peak at 1060 cm^{-1} gradually increases after thermal-oxidative reclamation, indicating that the cross-linking bonds in the waste rubber undergo different degrees of fracture as the reclamation time increases. The peak at 1733 cm^{-1} associated with C=O emerged after reclamation, whose intensity increases as the reclamation time increases. The emergence of C=O in RGTRs is a result of the oxidation and scission of the active allyl in the molecular chains of GTR.[34, 35] The possible reactions leading to the formation of carbonyl and sulfoxide groups are proposed in Figure 4. This process leads to the scission of macromolecular chains and hence partial destruction of the vulcanizate. The cleavage of a sufficiently large number of C=C bonds in

the vulcanized rubber results in the formation of oligomers. Therefore, the oxidative reclamation occurred in both main-chain and crosslink bonds during the reclamation process.

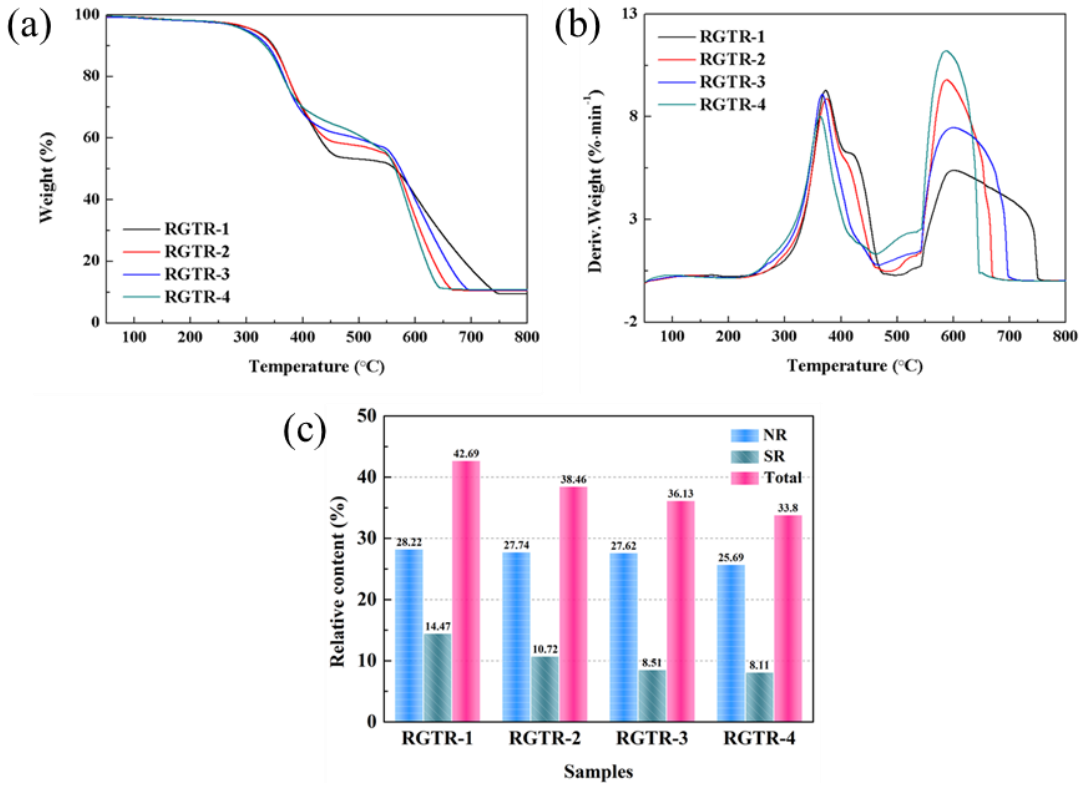

Figure 5. (a) TGA curves and (b) DTG curves for RGTR (c) The relative and total contents of NR, SR in the gels.

Thermal analysis of gel component of RGTRs

The presence of bound rubber in RGTRs was analysed by TGA and the results were shown in Figure 5. The first sharp degradation in the range of 370-410 °C observed for the four samples are mainly due to the decomposition of the rubber components. The low-temperature (approximately 375 °C) and high-temperature (approximately 410 °C) decompositions are consistent with the pyrolysis of NR and synthetic rubber (styrene-butadiene rubber and/or polybutadiene rubber), respectively.[36] The rubber content in the gel gradually decreases with the increase of the stirring time (Figure 5a), at the later stage where air atmosphere is activated, the CB can react with oxygen and causes weight loss at 563 °C. According to Figure 5b, the maximum decomposition temperature of CB in gel is

reduced from 660 °C to 580 °C due to the decomposition of the bound rubber. In addition, the presence of bound rubber leads to the maximum decomposition peak of CB splitting into two peaks, where the first one and the second one are associated with the decomposition of bound rubber and CB, respectively.[37, 38] According to the curves of TGA and DTG, the relative compositions of the gel are calculated and shown in Figure 5c, showing the relative content of NR and SR are obviously reduced as the degree of reclamation increases. Based upon this discussion, the reclamation process and mechanism is illustrated in Figure 6.

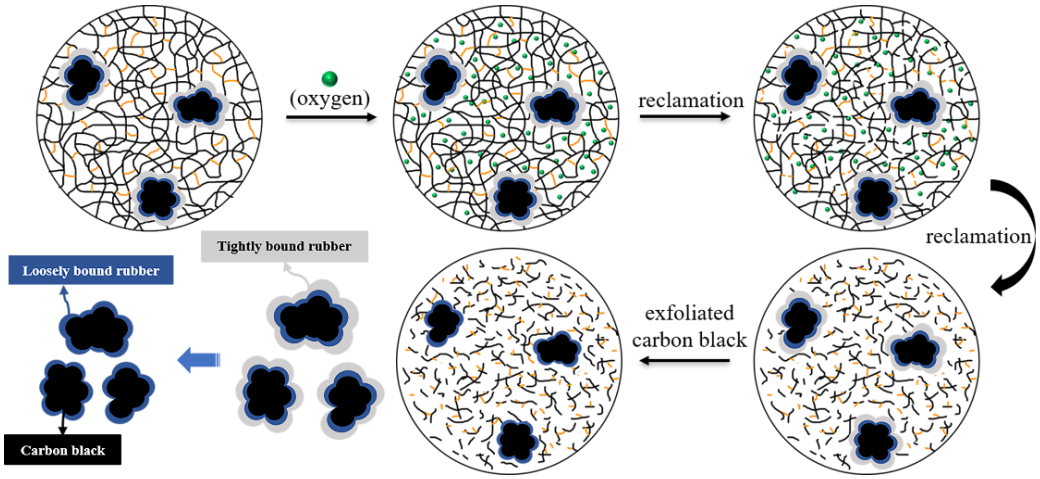

Figure 6. The schematic diagram showing the effect of oxygen in facilitating the dynamic thermal-oxidative reclaiming process.

Revulcanization of NR/RGTRs

The storage modulus (G′) versus the strain of uncured composites is shown in Figure 7, exhibiting a typical nonlinear relationship with strain increasing, which is generally called the 'Payne effect'.[39, 40] The Payne effect is considered to be a result of the breaking and reforming of physical bonds between the filler aggregates. The stronger the inter-filler interactions, the higher the strain amplitudes required to break down their networks, which results in a greater difficulty for of the fillers to disperse in the rubber matrix.

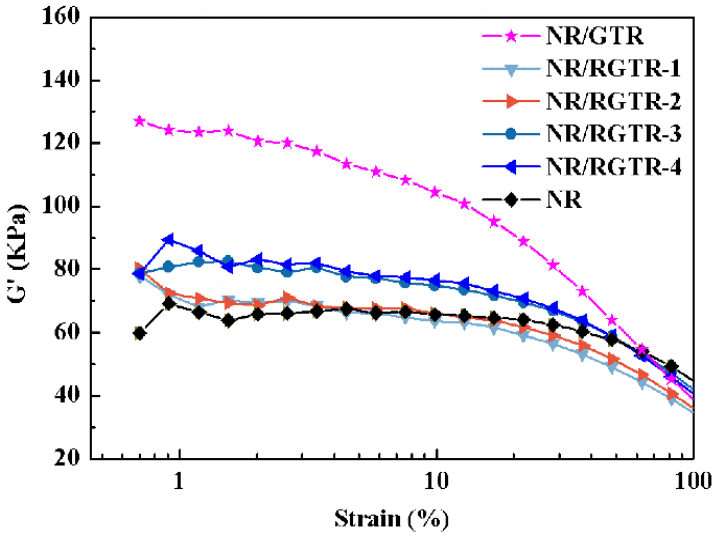

Figure 7. Payne effect of NR/RGTRs composites.

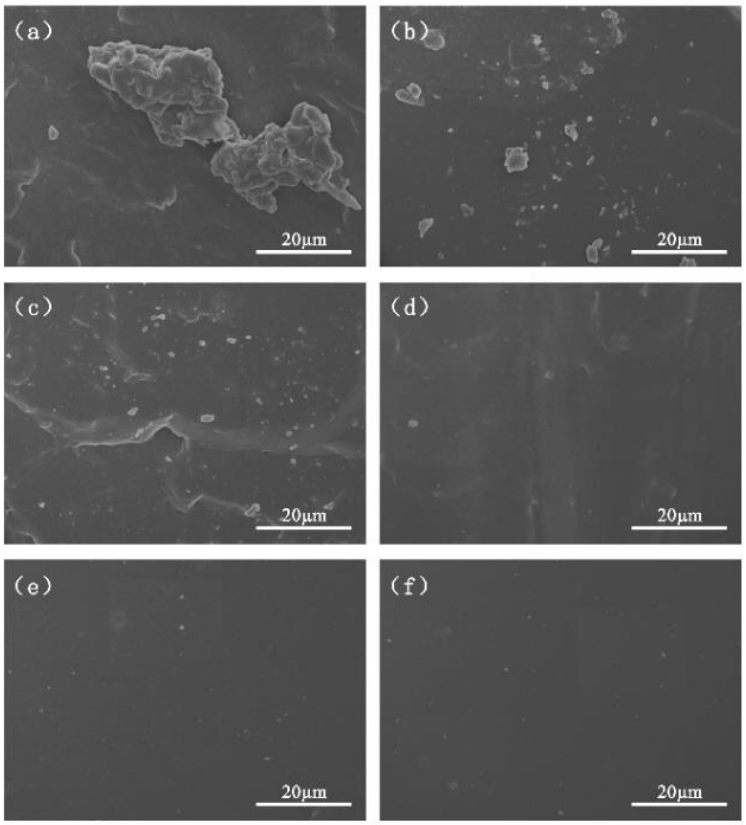

Figure 8. SEM micrographs of the fracture surface of the NR/RGTRs composites: (a) NR/GTR; (b) NR/RGTR-1; (c) NR/RGTR-2; (d) NR/RGTR-3; (e) NR/RGTR-4; (f) NR.

Since the reclaimed rubber contains a large amount of CB particles, it can be added to the NR matrix as a rubber-coated CB filler, so the dispersion of the RGTR in the NR can be measured by the Payne effect. It was observed from Figure 7 that the G′ of NR/RGTRs is obviously lower than that of NR/GTR, which is attributed to the destruction of the three-dimensional crosslinked structure. Through reclamation, the bound rubber coated CB particles are detached from the crosslinked rubber network, thereby improving the compatibility of the reclaimed rubber with the NR matrix and the dispersion of RGTR.

SEM micrographs of the cryogenically fractured surface of vulcanized NR and NR/RGTRs (Figure 8a-f) were taken to intuitively study the phase morphological structure and homogeneity of the vulcanizate. The GTR dispersed in the NR matrix in larger particulates because of their vulcanized structure, showing weak interaction between the substrates. From the micrographs, it is also evident that in samples with a higher degree of reclamation, the unfused gel particles in NR exhibit a reduced average particle size, showing a more homogeneous surface morphology. A nano-scale dispersion of RGTR-4 in the NR matrix can be observed, demonstrating the excellent compatibility between the RGTR-4 and NR matrix, which can be ascribed to the high amount of scission of the cross-linked structure. This result indicates the better recovery of mobility and plasticity of reclaimed rubber due to the increased structural breakage, suggesting that different reclamation levels had a significant influence on the vulcanized structures despite the same revulcanization process, which affects mechanical properties directly.

The strain-stress curves for vulcanizates of NR/RGTRs blends are shown in Figure 9. The NR/GTR blend shows the lowest tensile strength and elongation at break, which is due to the poor dispersion and weak interfacial adhesion between the GTR particles and matrix rubbers.

The highest mechanical properties are found in the blend of NR/RGTR-4, with a tensile strength of 19.34 MPa and an elongation-at-break of 757%. This is due to the loosely crosslinked network of the gel fraction of the RGTR-4 and strong interfacial adhesion between RGTR-4 and NR,

forming a continuous uniform network that is beneficial to the mechanical properties of the material. Any increase in tensile strength over that of untreated GTR is due to the improved interfacial adhesion resulting from network destruction.

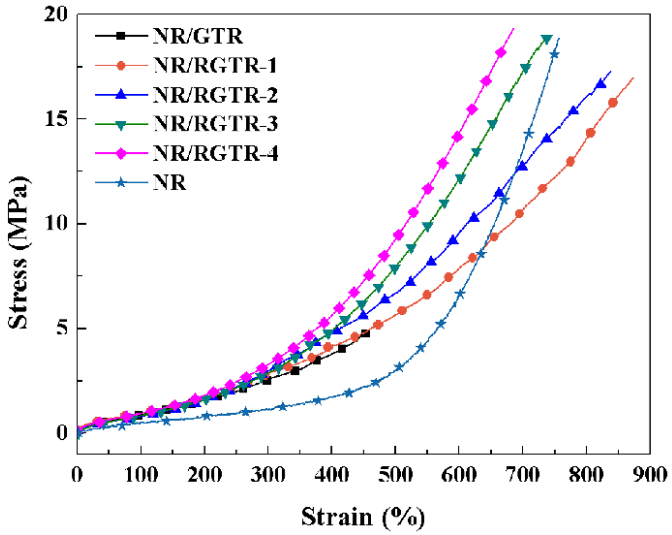

Figure 9. Strain–stress curves for revulcanized of NR/RGTRs.

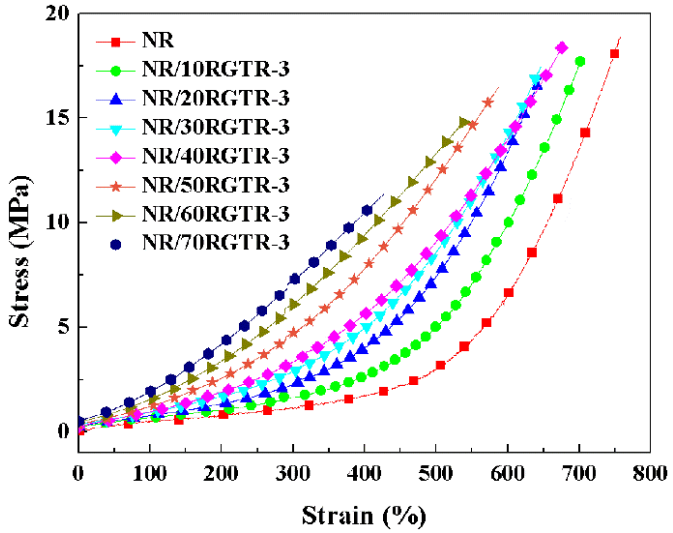

Figure 10. Stress-strain curves for revulcanized NR/RGTR-3 composites with various RGTR contents.

For efficient devulcanizing, it is crucial to break down the polymer network as much as possible before new polymer bonds are formed with the active radicals from chain fragments. Therefore, to avoid the

bonding reactions of reactive free radicals, the devulcanizing time should be as short as possible: in the current case RGTR-3 appears to be optimum.[41]

Table 3. Mechanical properties before and after aging

Samples	NR	NR/10RGTR-3	NR/20RGTR-3	NR/30RGTR-3	NR/40RGTR-3	NR/50RGTR-3	NR/60RGTR-3	NR/70RGTR-3
Tensile strength (MPa)	18.9	17.8	17.3	17.5	18.5	16.5	15.0	11.4
Standard deviation (MPa)	0.51	0.53	0.49	0.59	0.49	0.23	0.33	0.25
Elongation at break (%)	757	703	651	646	678	587	542	427
Stress at 100% elongation (MPa)	-	0.68	0.74	0.94	0.97	1.22	1.56	1.92
Stress at 300% elongation (MPa)	-	1.64	2.16	2.88	3.35	4.72	6.11	7.25
Air oven aging（100 °C × 48 h）								
Tensile strength (MPa)	8.8	11.7	10.7	11.7	13.0	9.7	9.6	7.6
Standard deviation (MPa)	0.42	0.42	0.43	0.44	0.31	0.40	0.2	0.15
Elongation at break (%)	556	538	517	476	392	294	252	180
Stress at 100% elongation (MPa)	0.52	0.71	0.81	1.05	1.61	1.93	2.48	3.60
Stress at 300% elongation (MPa)	1.38	2.25	2.91	4.31	7.13	-	-	-

The stress-strain curves and specific data for NR/RGTR-3 vulcanizates with various proportions of RGTR are shown in Figure 10 and Table 3. Compared to that of the NR vulcanizates, no significant difference was observed in the tensile strength of vulcanizates filled with increasing RGTR content from 10-40 wt%. However, a drop in the tensile strength from 18.5 MPa to 11.4 MPa was observed as the concentration of RGTR in the composite was increased from 40 wt% to 70 wt%. These trends are quite surprising, as a sustained decline in tensile strength should normally take place. It is well known that the properties of rubber are controlled by the nature and the degree of crosslinks in the network and filler-

polymer interactions. The apparent similarity between tensile stress of pure NR and 40 wt% RGTR is possibly due to the relatively low RGTR content, which can effectively reduce the negative effects caused by main chain reclamation. On the other hand, the residual CB, stripped from the bound rubber by dynamic thermal-oxidative reclamation can incur extra reinforcement. As a result, a roughly constant tensile strength can be reached. Additional RGTR content (>40 wt%) harms the elongation at break values due to the increased amount of shorter molecular chains, for which the CB of RGTR is not concentrated enough to maintain tensile strength. The minimum value was reached at 70 wt% RGTR content.

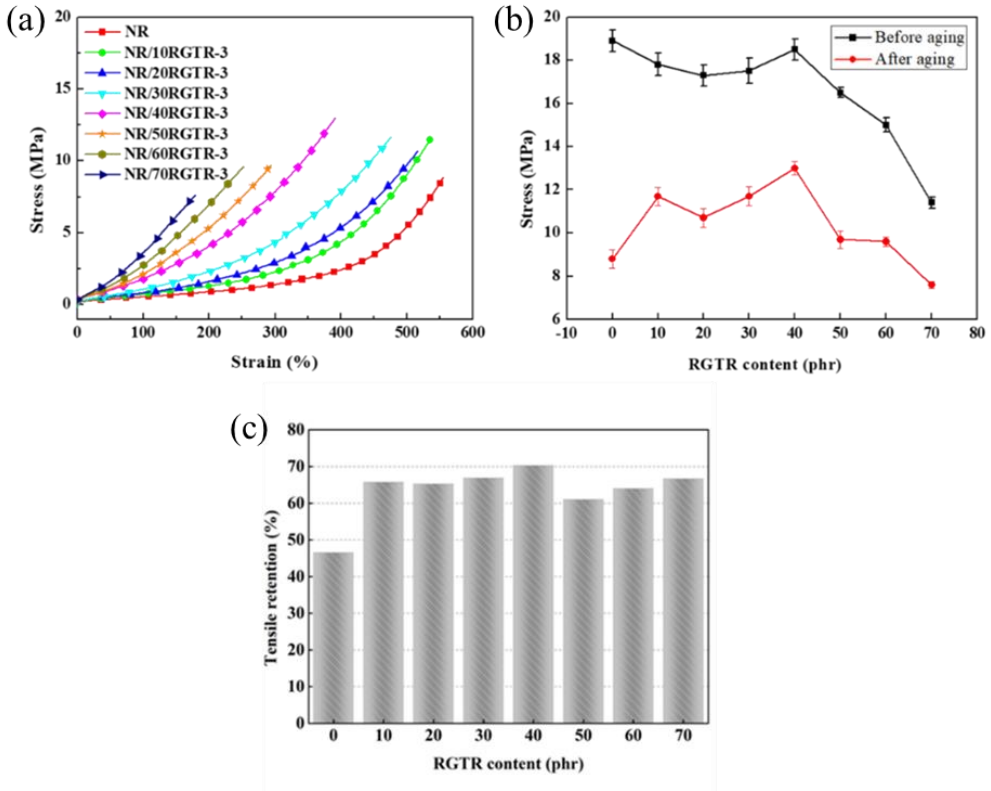

Figure 11. (a)Stress–strain curves for NR/RGTR-3 revulcanizates after aging, (b) Tensile strength of NR/RGTR-3 revulcanizates as a function of RGTR content, (c) Tensile retention of NR/RGTR-3 revulcanizates as a function of RGTR content.

The aging characteristics of the rubber composites containing reclaimed rubber were evaluated by accelerated aging tests (Table 3). From Figure 11a, it is evident that both the 100 and 200% modulus increase with an increase in the proportion of reclaimed rubber during aging. This is because reclaimed rubber may contain some active crosslinking sites that form crosslink bonds during aging. Evolutions of tensile strength after aging (red line) are compared to those obtained before thermal aging (black line) in Figure 11b. In all cases, the tensile strength decreased after aging. It can be seen that tensile retention of the material increases as the quantity of RGTR increases, which means that the blends become more aging resistant with the RGTR content. A plausible explanation is that double bonds are prone to breakage in the presence of oxygen during aging, which results in lower tensile retention. However, the initial presence of the anti-aging agent and CB in the waste tires induced a good aging resistance of the blends and a lower content of double bonds in the RGTR that reduces the thermo-oxidative aging reaction. This phenomenon shows some antiaging characteristics of RGTR, suggesting that the use of antioxidants may be reduced or even entirely excluded if RGTR is used in product formulation.

CONCLUSIONS

This work demonstrates an environmentally-friendly and effectively dynamic thermal-oxidative reclamation process for recycling waste rubbers. High reclamation degree of GTR (sol fraction 66.53 wt%) was obtained using a dynamic thermal-oxidative reclamation reactor at 200 °C for 20 min in air, without involving any reclaiming agents. Oxidative reclamation induced crosslink breakage and main chain scission simultaneously, destroying the crosslinked network of the GTR, which led to an increase in the sol fraction and a decrease of the molecular weight. Due to the high reclamation degree, the CB can be separated from the crosslinked network of GTR and be extracted into the sol part. The RGTR with high reclamation degree showed good dispersibility and reinforcing in NR compared with other traditional reclaimed rubber. The addition of 10 to 40 wt% of RGTR in NR had no adverse effect on the mechanical properties, instead improved the aging resistance of NR.

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Notes

The authors declare no competing financial interest.

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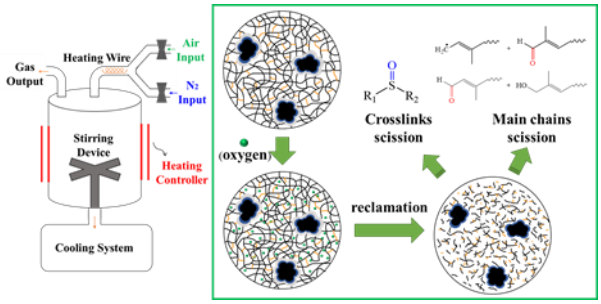
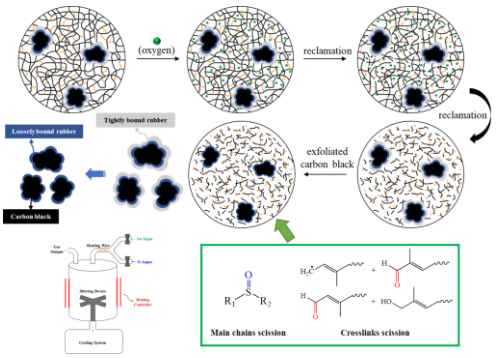
SYNOPSIS. This work introduces a feasible and environmentally-friendly method for the preparation of reclaimed ground tire rubber with high-performance.

Abstract Graphic.




(oxygen)
reclamation
reclamation
exfoliated
carbon black
Loosely bound rubber
Tightly bound rubber
Carbon black
Main chains scission
Crosslinks scission